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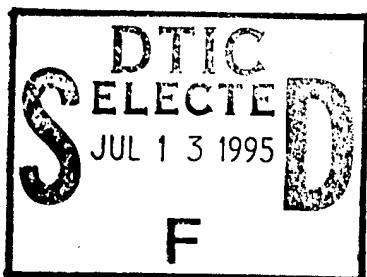
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R & T Code 313T006

Technical Report #17

Visible Light Photopolymerization: Synthesis of New Fluorone Dyes and
Photopolymerization of Acrylic Monomers Using Them

Tanabe, T.; Torres-Filho, A.; Neckers, D.C. *J. Poly. Sci., Chem. Ed.* in press.



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Date Submitted
June 15, 1995

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED		
	6-15-95	Technical Report		
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS		
Visible Light Photopolymerization: Synthesis of New Fluorone Dyes and Photopolymerization of Acrylic Monomers Using Them		G N00014-93-J-1921 R & T 313T006		
6. AUTHOR(S)		Kenneth Wynne		
D.C. Neckers				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION REPORT NUMBER		
Center for Photochemical Sciences Bowling Green State University Bowling Green, Ohio 43402		17		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000				
11. SUPPLEMENTARY NOTES				
Tanabe, T.; Torres-Filho, A.; Neckers, D.C. <i>J. Poly. Sci., Chem. Ed.</i> in press.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE		
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13. ABSTRACT (Maximum 200 words)				
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14. SUBJECT TERMS		15. NUMBER OF PAGES		
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified		Unclassified	Unclassified	UL

Visible Light Photopolymerization: Synthesis of New Fluorone Dyes and Photopolymerization of Acrylic Monomers Using Them

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ABSTRACT: Several 3-alkoxy-5,7-diodo-6-fluorones ($\lambda_{\text{max}} \approx 470$ nm) have been synthesized and evaluated as initiators for photopolymerization triggered with the 515.5 nm line of an Ar⁺ laser. 2-Acyl and 2-alkyl-4,5,7-triiodo-3-hydroxy-6-fluorones were also tested at 515.5 nm. 9-Cyano-2-acyl- and 9-cyano-2-alkyl-4,5,7-triiodo-3-hydroxy-6-fluorones were studied and could be excited with the 632 nm line of a He-Ne laser. Dyes with long linear carbon chain alkoxy groups at C-6 showed larger molar extinction coefficients and formed polymers with better mechanical properties than did compounds with shorter carbon chains, or did the corresponding C-6 phenols. The optimum side chain length of the C-6 ether alkyl group is between 4 to 7 carbon atoms. With longer carbon chain alkoxy groups at C-8, e.g., octyl, the mechanical properties of the formed polymers are inferior to systems formed with the butyl isomer as photoinitiator. In the case of alkoxy groups with branched alkyl groups (e.g. 2-ethylbutyl), the relationship between dye structure and the properties of the polymers formed is less straightforward. Though the dyes react from their triplet state, the fluorescence quantum yields of the dyes and the performance of the dyes as photoinitiators appear directly related.

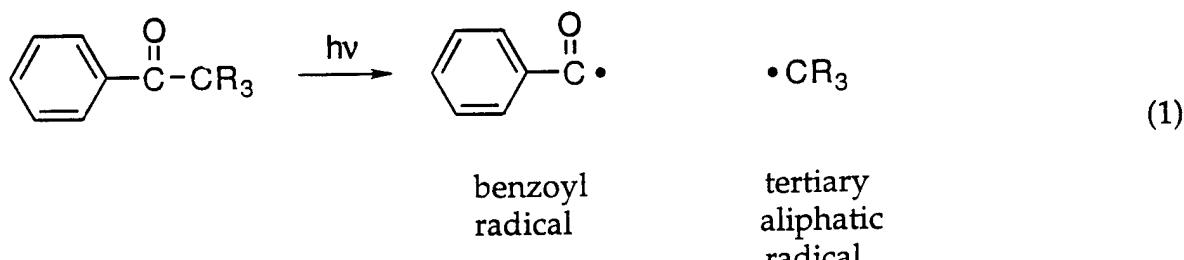
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Introduction

The introduction and use of visible light photoinitiators, compounds which absorb from 400 nm to 800 nm and initiate radical or cationic polymerization in the presence of certain coinitiators, has taken on significant importance in recent years. Visible systems provide photocure in a friendlier manufacturing environment than do commonly used uv radiation cure alternatives. Since visible initiators often bleach as they generate reaction intermediates, cures can be effected at much greater depth, in pigmented or colored environments because virtually all pigments and dyes are uv opaque but have regions of transparency in the visible region of the spectrum, and employ much simpler light sources than do comparable uv cure ensembles. A simple overhead projector bulb also suffices to initiate polymerization with visible light sensitive formulations. Many visible systems are now part of commercial products. These include the positively charged cyanine dyes and anionic borate salts used with polyolacrylates in Mead Imaging's photopolymer color copying system, Cyclicolor[®]³, the camphor quinones which are used for the polymerization of reconstructive dental materials and certain adhesives⁴, and a number of experimental formulations using the titanocenes⁵, ferrocinium salts, or other compounds⁶ as the light absorbing species which catalyze photopolymer formation.

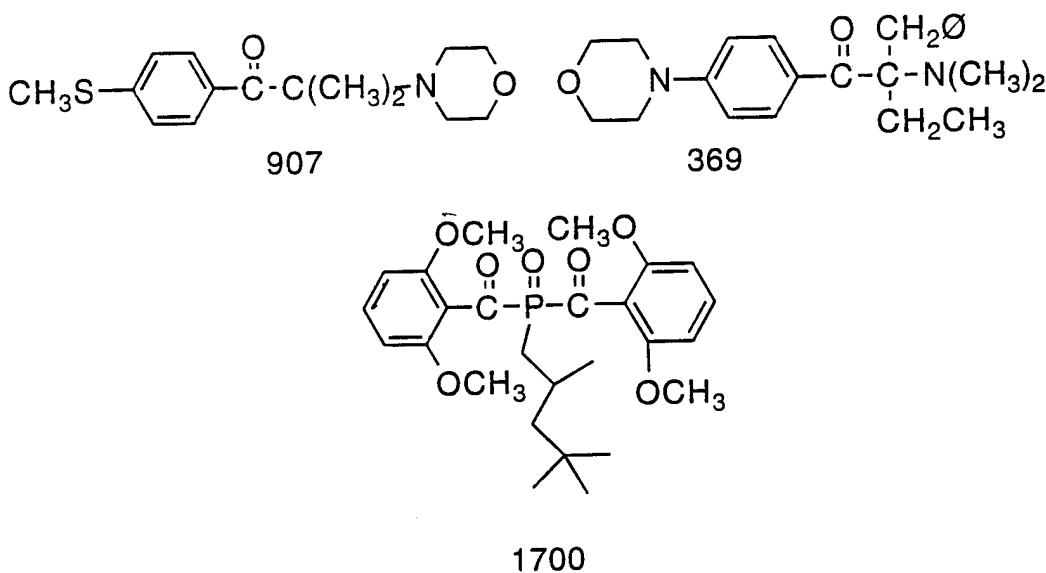
The original and major commercial photoinitiators used for the polymerization of vinyl monomers like acrylates and unsaturated polyesters are still sold in largest volume and are of two types; those which initiate radical chains after a bond dissociation reaction, so-called Type I initiators because most function by a reaction which is equivalent to the Norrish Type I split of ketones,⁷ and photoinitiators which generate radicals after an oxidation/reduction process. Most uv initiators such as the acetophenone ketals, benzoin ethers, and phosphine oxides are of the former type. Several critical photophysical and structural parameters predict effective dissociation of an aromatic ketone into a partner pair of radicals, (1), and quantum yields for dissociation are highest for compounds in which at least one

group attached to the carbonyl group is trisubstituted. Most commercial bond dissociation photoinitiators have this common structural feature.



The $n-\pi^*$ transition of most ketones, occurring in the mid uv, is weak ($\epsilon \approx < 1000$). In order to obtain sufficient optical density for effective photopolymerization performance in monomer formulations at the lines of the mercury resonance lamp, common commercial photoinitiators are often used in immense (generally over 1% by weight in monomer mixtures) concentrations. Since most aromatic ketones intersystem cross to the triplet state with unit quantum efficiency (another critical structural parameter), and triplet lifetimes are generally quite short (a few nanoseconds) in non-reactive solvents, all uv photoinitiators arrive at the radical pair derived from homolytic dissociation unimpeded by any component of the formulation. A critical point is that with the exception of aromatic monomers such as styrene most monomers react slowly, if at all, with the triplet state of most ketones, and thus have a limited effect on the performance of the initiators in formulations; i.e. there is little or no quenching of initiator triplets by the monomers. Individual Type I initiators have been designed to meet specific performance criteria in individual polymer systems. Among critical specifications which the product polymer must meet are the character of the surface of polymer formed from by the photopolymerizing system in which the initiator is used, the photospeed in the formulation, and the modulus of the formed solid. Often an important issue is the residual color of the matrix formed after photopolymerization. Thus since the concentration requirements of uv initiators are high, most have been targeted at the short wavelength lines of mercury light sources (313 nm and 366 nm)

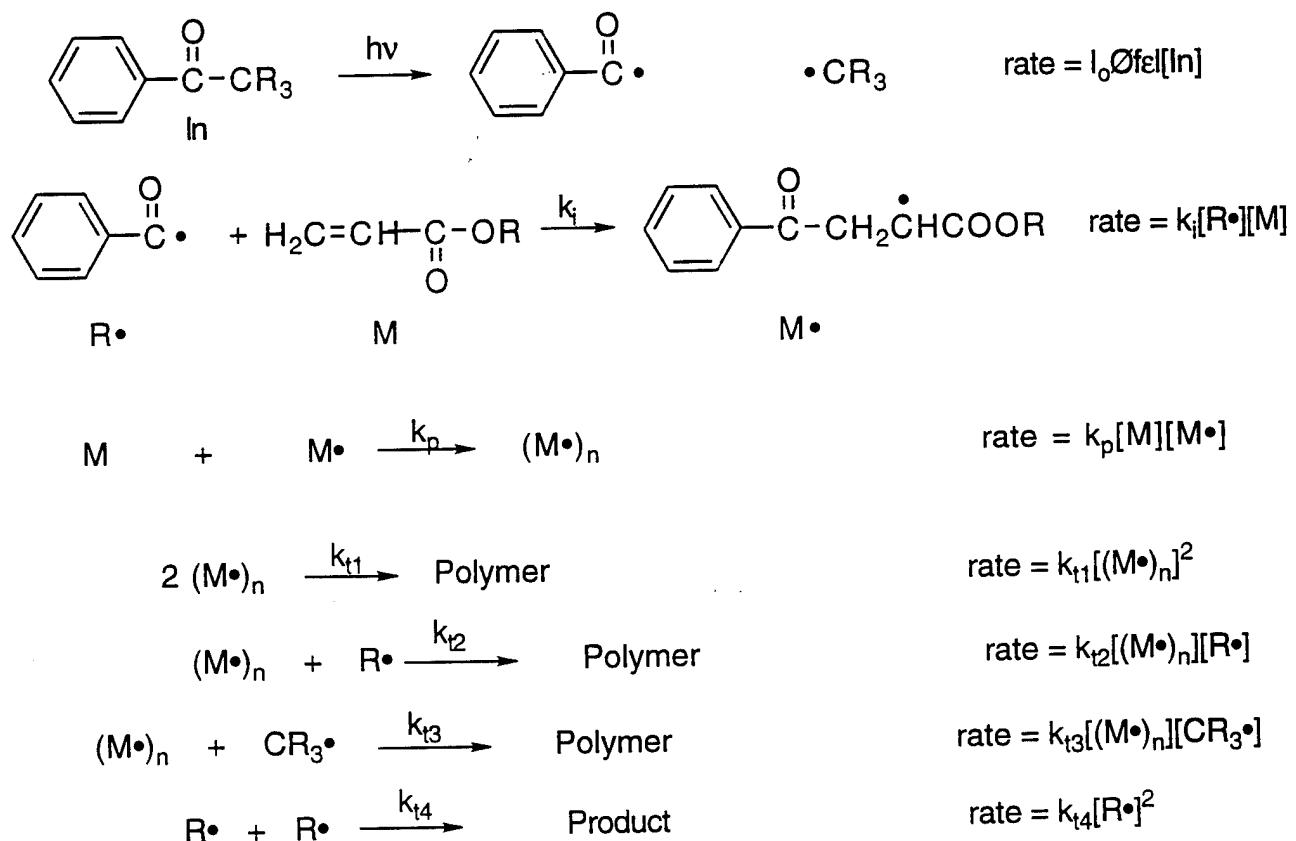
and produce generally colorless formulations and photopolymers. Recently certain longer wavelength absorbing uv initiators (λ_{max} 360-390nm) have appeared commercially. As examples we cite 2-methyl-1[4-(methylthio)phenyl]-2-morpholinopropanone-1 {Irgacure 907}, 2-benzyl-1[4-(morpholino)phenyl]-2-dimethylaminobutanone-1 {Irgacure 369}, and bis (2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide {CGI 1700}. In each case substantial charge transfer from the electron donating aromatic substituents on the aromatic ring causes a red shift in the maximum absorption and an increase in the extinction coefficient for the transition.



To incur stability to the alkyl radical formed upon photodecomposition (*vide infra*) of a ketone by the Type I process, tertiary substitution is more or less mandatory. This substitution pattern also has the effect of decreasing reactivity of the formed radical. Thus, though 369, 907 and 1700 (*vide supra*) have benzoyl radicals in common, the radical moieties formed from the aliphatic carbon of the ketone in cases of 369 and 907 are relatively stable and thus unreactive. These highly substituted radicals are ineffective initiators (i. e., the rate of their addition to olefinic double bonds is relatively slow), but they are also relatively unreactive as chain

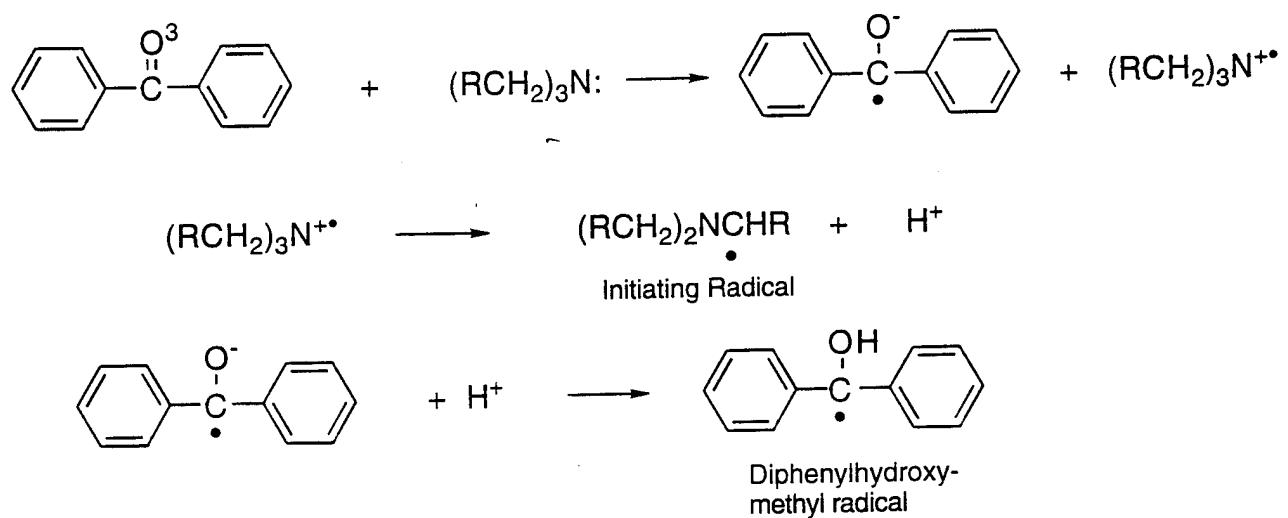
terminators. Since the rate of polymerization of a vinyl monomer under steady state conditions is directly proportional to the rate of initiation and inversely proportional to the rate of chain termination, and the initiating radical is probably the same in every case, lower chain termination rates of the partner aliphatic tertiary carbon radicals are likely at least one of the important means by which specific uv photoinitiators differ in performance.

The chain process for the polymerization of a simple acrylate initiated with a bond dissociation aromatic ketone photoinitiator (1) is shown below: if the dissociation rates of two initiators are comparable, the only reaction which differs from case to case is termination with the partner aliphatic ketone tertiary radical ($\cdot\text{CR}_3$ in the scheme).



There are also several commercial examples of photoinduced single electron transfer processes (so-called oxidation/reduction initiators) which lead to radical

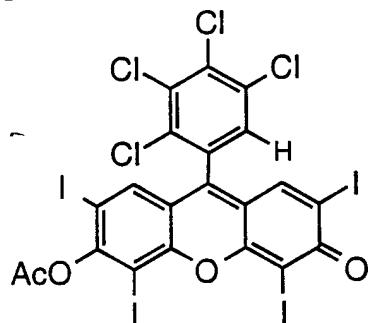
formation and subsequent polymerization. There are also examples of oxidation/reduction initiators used with uv light sources which include benzophenone/tertiary amine systems and camphor quinone/tertiary amine systems. In the benzophenone/tertiary amine system, for example, benzophenone triplet state is reduced by the tertiary amine producing the radical anion of benzophenone and radical cation of the amine. The latter loses a proton forming the initiating radical, (see below). The diphenylhydroxymethyl radical, being notoriously unreactive, permits relatively long chains to grow in its presence. What's more, radical formation by oxidation/reduction is generally critical for the initiation of polymerization with visible light.



The thermodynamic spontaneity of electron transfer processes are, to the first approximation, predicted by the electrochemical potentials of the acceptor in oxidizing a potential electron donor and the donor in reducing any potential electron acceptor. Whenever a donor or acceptor reacts from an excited state it is made either more reducing or more oxidizing by an energy equivalent to the excited state energy of the reacting state. In contrast to the situation with bond dissociation initiators, where all the energy for free radical formation must be provided by the light

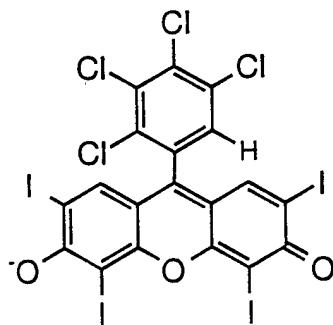
absorption process, electron transfer systems also benefit from the inherent potential of donor and the acceptor for electrochemical change.

Initiators for the polymerization of acrylate monomers with visible light were first reported by Oster⁸ who described three series of dyes as being 'photoreducible'; the acridines, the xanthenes and the thiazenes. Coinitiators were required as reducing agents in Oster's applications and included the above mentioned tertiary amines, or ascorbic acid.⁹ Several patents resulted from this work¹⁰ as did gel electrophorsis. Among Oster's initiators were the xanthenes such as Eosin, Rose Bengal or erythrosin which have two negatively charged centers. These are not especially soluble in most monomer mixtures so a critical development in their utility as photoinitiators was the report of 3-acetoxy-9-(2',3',4',5'-tetrachlorophenyl)-



2,4,5,7-tetraiodo-6-fluorone, [RBAX]

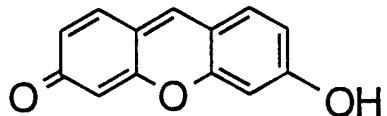
a monomer soluble derivative with spectral properties resembling those leuco (actually orange) Rose Bengal¹¹. RBAX, after single electron transfer from tertiary amines or triarylalkyl borates, loses an acetoxy radical about 10% of the time in a reaction which forms a deep red absorbing dye with a chromophore not unlike that of Rose Bengal. This permits easy following of the photoreduction reactions by spectroscopic means.



In studying RBAX and various analogs, Shi¹² postulated that since electron transfer from donor to dye triplet state was a bimolecular process, steric inhibition in the large, bulky RBAX could significantly retard the approach of an electron donor such as an aromatic tertiary amine to the site to be reduced. He chose to synthesize a series of dyes without the bulky C-9 aromatic substituent, the hydroxyfluorones, which are becoming benchmarks.

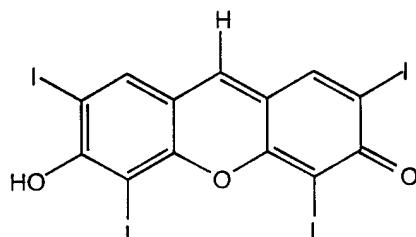
Synthetic fluorone dyes are developing an active, practical role in new applications of visible light sensitive materials¹³ since, with visible light, greater depth of cure can be achieved due to the bleaching of the dyes. The intrinsic transparency of most monomers and oligomers to visible radiation^{9,10} increases the promise the fluorones hold in applications requiring enhanced performance characteristics in pigmented systems or in formulations containing uv absorbers.

The generic fluorone on which the series is based is 3-hydroxy-6-fluorone



3-hydroxy-6-fluorone

Its skeleton is the parent heterocyclic skeleton of the xanthene dye, fluorescein. Derivatives halogenated on the aromatic ring such as

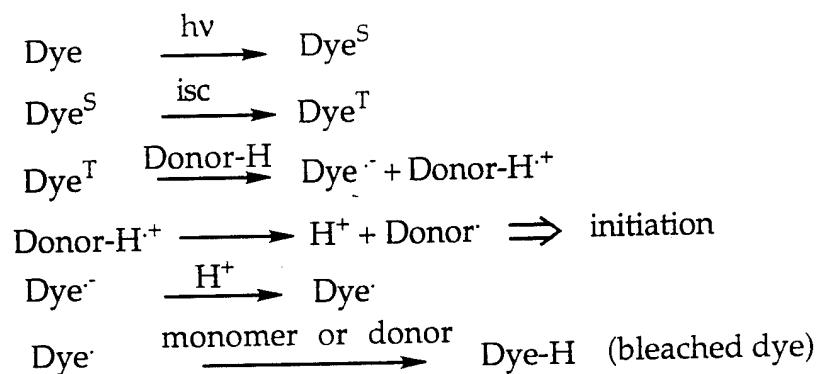


2,4,5,7-tetraido-3-hydroxy-6-fluorone (TIHF)

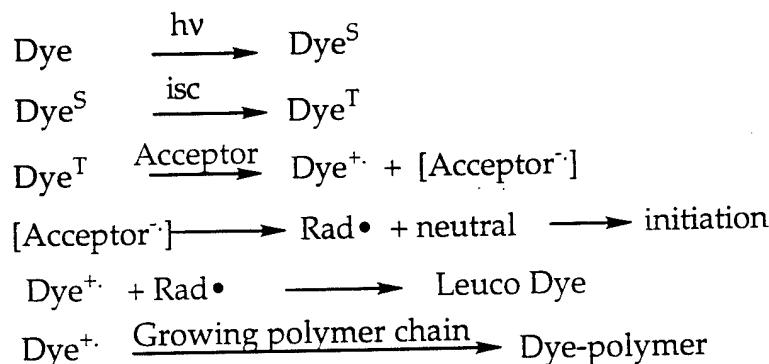
initiate

free radical polymerization when amines are used as coinitiators via a photoreduction process⁹. Scheme 1 shows the accepted mechanism of dye reaction by a photoreduction process. The reactive excited state of the fluorone is the triplet state¹⁴ to which one electron is transferred from the amine with a bimolecular rate constant of about 10^7 sec⁻¹. The process forms an amino cation radical and the dye anion radical. The former rapidly releases a proton yielding a neutral radical in a pH

dependent process and it is this radical which initiates the polymerization. The partner dye anion radical accepts a proton forming the dye radical. This dye radical couples or abstracts a hydrogen from monomer forming the so called "leuco type" reduced structure.¹⁵ Fluorones also initiate polymerization in the presence of onium salts via photooxidation processes^{16,17}. Though the overall mechanism of this process is understood somewhat less completely, the ultimate result is the rapid formation of free radicals which initiate polymerization from the capturing of the excited state of the dye by electron transfer from, rather than to, the heteroaromatic nucleus, Scheme 2.



Scheme 1

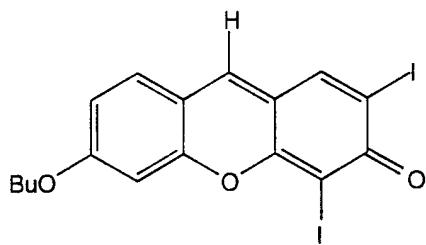


Scheme 2

We have recently reported that among the various fluorone dyes, 3-ethoxy-5,7-diiodo-3-fluorone (DIEF) forms network polymers with superior mechanical properties¹⁸ to those formed from photopolymerization with other dyes formed with

an Ar⁺ laser. The mechanical properties of the formed polymer initially tended to improve with an increase in dye concentration. However, as the concentration of dye was increased beyond a certain point (in the case of DIEF somewhere between 1x10⁻³ and 5x10⁻³M) there was some indication of non-solubilized particle aggregation, and the mechanical properties of the formed photopolymer decreased dramatically.

We report herein the synthesis of several new 3-alkoxy-5,7-diiodo-6-fluorones, and on the mechanical aspects of the photopolymers formed from multifunctionalized polyolacrylates with the most promising of them, 3-butoxy-5,7-



diiodo-6-fluorone.

The work is part of our continuing

effort to (1) develop photoinitiators whose photospeed can be controlled which produce functional polymeric materials with visible light; and (2) understand the relationship between the photochemistry/photophysics of the dye and the properties of polymers formed from using them.

Experimental Section:

Materials:

All solvents were purchased from Aldrich Chemical Co. and used as received. Other chemicals save 3,6-dihydroxyxanthone were purchased from Aldrich Chemical or Fisher Co. 3,6-Dihydroxyxanthone was purchased from Hilton-Davis Co., or from Norquay, Inc., and was purified as follows: commercial 3,6-dihydroxyxanthone was dissolved in an aqueous solution of 5% sodium hydroxide. The solution was filtered and the corresponding xanthone was then formed by controlling the pH at 8.8-9.2 by adding hydrochloric acid to the filtrate. The resulting precipitate was filtered, washed successively with water, with dilute hydrochloric acid and with water again.

¹HNMR (DMSO): δ 10.87 ppm (2H, s), 8.00 (2H, d, 8.5Hz), 6.82-6.94 (4H, m)

MS m/e for C₁₃H₈O₄ calcd 228.20 measured 228.20

Synthesis of 3-alcoxy-5,7-diiodo-6-fluorones

3-Ethoxy-5,7-diiodo-6-fluorone (DIEF) was synthesized according to our previously reported procedure¹². Other dyes were synthesized according to Scheme 4. Details of the synthetic procedures follow:

Synthesis of 3-butoxy-6-hydroxyxanthone (1a)

3,6-Dihydroxyxanthone (0.8mol) was dissolved into hot basic water (Na₂CO₃ {2.56 mol} in 3.6 l of water and 130 ml of 2-propanol) and the temperature was controlled at 70°C. Butyl bromide (2.4 mol) was added dropwise and the resulting mixture stirred vigorously for 46 hours after which the resulting white precipitate was filtered and washed with water several times. There was almost no disubstituted compound (3,6-dibutoxyxanthone) in the product. The precipitate was dissolved in 3% NaOH, filtered and reprecipitated with HCl; Yield: 81.4% 3-butoxy-6-hydroxyxanthone.

¹HNMR (DMSO): δ 8.04 ppm (1H, d, J=8.8Hz), 8.01 (1H, d, 8.8Hz), 7.07 (1H, d, 2.3Hz), 6.99 (1H, dd, 8.8Hz, 2.4Hz), 6.89 (1H, dd, 8.6Hz, 2.2Hz), 6.84 (1H, d, 2.1Hz), 4.13 (2H, t, 6.3Hz), 1.6 (2H, m), 1.3 (2H, m), 0.94 (3H, t, 6.8Hz)

MS m/e for C₁₇H₁₆O₄ calcd 284.31 measured 284.20

Synthesis of 3-butoxy-6-hydroxyxanthane (2a)

3-Butoxy-6-hydroxyxanthone (760 mmol) was suspended in 500ml of anhydrous THF to which was added 1.6 mol of 1N BH₃·THF at room temperature. The reaction mixture was then stirred at 60°C for 2 hours. After adding HCl (1.0N) until the bubbling ceased, 300ml of water was added and the THF removed leaving a precipitate which was filtered and washed with water. The precipitate was redissolved in dilute NaOH and precipitated with dilute HCl. This precipitate was

filtered, washed with water and dried in a vacuum oven at 50°C. 3-Butoxy-6-hydroxyxanthane was obtained quantitatively.

^1H NMR (CDCl_3): δ 7.03 ppm (1H, d, $J=8.7\text{Hz}$), 7.01 (1H, d, 8.9Hz), 6.49-6.64 (4H, m), 4.76 (1H, s), 3.95 (2H, t, 6.3Hz), 3.90 (2H, s), 1.5 (2H, m), 1.0 (2H, m), 0.98 (3H, t, 7.3Hz)
MS m/e for $\text{C}_{17}\text{H}_{18}\text{O}_3$ calcd 270.33 measured 269.95

Synthesis of 3-butoxy-5,7-diiodo-6-fluorone (3a)

3-Butoxy-6-hydroxyxanthane (1.03 mol) and iodine (1.03 mol) were dissolved in 3.05 l of methanol. An aqueous solution of iodic acid (1.13 mol of HIO_3 in 200 ml of water) was added dropwise into the reaction mixture at room temperature followed by stirring for 2 hours at 55°C. The resulting precipitate was filtered and washed with methanol, with water, and with methanol again. The yield of 3-butoxy-5,7-diiodo-3-fluorone was 91.3%.

^1H NMR (CDCl_3): δ 8.12 ppm (1H, s), 7.72 (1H, s), 7.58 (1H, d, 8.8Hz), 7.06 (1H, d, 2.4Hz), 6.98 (1H, dd, 8.7Hz , 2.4Hz), 4.14 (2H, t, 6.4Hz), 1.9 (2H, m), 1.6 (2H, m), 1.02 (3H, t, 7.3Hz)
MS m/e for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{I}_2$ calcd; 520.10 measured; 520.25.

Synthesis of 9-Cyano-3-butoxy-5,7-diiodo-6-fluorone (4a)

DIBF (2 mmol) and KCN (6 mmol) in dry DMF (10 ml) were stirred at room temperature. After 2 hours, the reaction mixture turned deep green. Formic acid (1ml) was added (carefully!) upon which the reaction mixture turned red-purple. The solution was stirred for 3 more hours, then poured into water, extracted with dichloromethane, washed with water, the dichloromethane was removed under reduced pressure and the residue purified by column chromatography (hexane/ethyl acetate). The yield of 9-cyano-3-butoxy-5,7-diiodo-6-fluorone was 54%.

^1H NMR (CDCl_3): 8.48 ppm (1H, s), 7.83 (1H, d, 9.5Hz), 7.05-7.09 (1H, m), 7.04 (1H, s), 4.16 (2H, t, 6.5Hz), 1.8-1.9 (2H, m), 1.5-1.6 (4H, m), 1.02 (3H, t, 7.3Hz)

b) Synthesis of 2-acyl or 2-alkyl-4,5,7-triiodo-6-fluorones

The syntheses of all 2-acyl or 2-alkyl-4,5,7-triiodo-6-fluorones were performed by following Scheme 4. Octanoyl chloride was used for the Friedel-Crafts acylation reaction.

Synthesis of 3,6-Dimethoxyxanthone (5)

3,6-Dihydroxyxanthone (100mmol) was dissolved in 350 ml NaOH [1.14 M]. To the solution was added dimethyl sulfate (400 mmol) dropwise and the mixture was stirred for 5 hours at 60°C. The resulting precipitate was filtered, washed with aqueous NaOH and then with water. The yield was 72.9%.

^1H NMR (CDCl₃): 8.23ppm(2H, d, 8.8Hz), 6.93(2H, dd, 8.8Hz, 2.6Hz), 6.85(2H, d, 2.6Hz), 3.93(6H, s)

Alternatively: In 100ml of an aqueous solution of sodium hydroxide (2.2%) was dissolved 36.5mmol of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone. The solution was refluxed for 72 hours to form a precipitate which was filtered and washed with water. The yield of 3,6-dimethoxyxanthone 94.5%.

Synthesis of 3,6-Dimethoxyxanthane (6)

3,6-Dimethoxyxanthone (50.7 mmol) was suspended in 70ml of THF. To the suspension was added, dropwise, 52.0 ml of 1N BH₃·THF at room temperature followed by stirring for 2 hours at 60°C. After the stirring was complete, dilute HCl (1N) was added until bubbling ceased, 30ml of water was added and the THF was removed under reduced pressure. The residual solid was filtered and washed with water yielding 99.1% of 3,6-dimethoxyxanthane.

^1H NMR (CDCl₃): 7.05ppm(1H, d, 8.8Hz), 6.62(1H, dd, 8.8Hz, 2.6Hz), 6.60(1H, s), 3.92(2H, s), 3.80(6H, s)

Synthesis of 2-Octanoyl-3,6-dimethoxyxanthane (7: R=n-C₇ H₁₅)

3,6-Dimethoxyxanthane (8mmol) and octanoyl chloride (8mmol) were dissolved in 30ml of anhydrous dichloromethane and the solution was cooled to -30°C with

dry ice in ethanol. Aluminum chloride (10mmol) was added to the solution and the temperature was gradually elevated to room temperature. After stirring for 2 hours, the mixture was cooled again in a dry ice/ethanol bath. HCl (1N, 40ml) was added dropwise to destroy the remaining aluminum chloride, the organic compounds extracted with dichloromethane and the extract washed with water several times. The dichloromethane was removed under reduced pressure. The crude solid was dissolved in hot hexane and allowed to cool gradually, to give the recrystallized 2-octanoyl-3,6-dimethoxyxanthane (mp = 87.0°C) in 78.7% yield.

^1H NMR (CDCl₃): 7.62ppm(1H, s), 7.07(1H, d, 8.3Hz), 6.6-6.7(1H, m), 6.61(2H, s), 3.93(2H, s), 3.90(3H, s), 3.81(3H, s), 2.94(2H, t, 7.3Hz), 1.6-1.8(2H, m), 1.2-1.4(8H, m), 0.90(3H, t, 6.6Hz)

MS m/e for C₂₃H₂₈O₄ calcd 368.47 measured 368.15

Synthesis of 2-Octanoyl-3,6-dihydroxyxanthane (8: R=n-C₇ H₁₅)

2-Octanoyl-3,6-dimethoxyxanthane (1.47mmol) and 5ml of ethanethiol were dissolved in 20ml of anhydrous dichloromethane. The mixture was cooled to -15°C in salt/ice bath. After aluminum chloride (7.5mmol) was added, the mixture was stirred overnight at room temperature. The reaction mixture was subsequently poured into a mixture of 20g of ice and 10ml of conc. HCl. The resulting precipitate was dissolved in NaOH aqueous solution and reprecipitated in dilute HCl. The precipitate was finally filtered and washed with water to yield 85.2% of 2-octanoyl-3,6-dihydroxyxanthane.

^1H NMR (DMSO): 12.25ppm(1H, s), 9.58(1H, s), 7.87(1H, s), 7.06(1H, d, 8.3Hz), 6.58(2H, s), 6.50(1H, d, 8.5Hz), 3.89(2H, s), 3.03(2H, t, 7.1Hz), 1.5-1.7(2H, m), 1.2-1.4(8H, m), 0.87(3H, t, 6.4Hz)

Synthesis of 2-Octanoyl-4,5,7-triiodo-3-hydroxy-6-fluorone (9: R=n-C₇ H₁₅)

2-Octanoyl-3,6-dihydroxyxanthane (0.988mmol) and I₂ (2.0mmol) were dissolved in 10ml of ethanol. An aqueous solution of HIO₃ (2.0mmol in 0.5ml of water) was added and the mixture was stirred for 1 hour at room temperature and 2 hours at

reflux. The resulting red solid was filtered and washed with ethanol, water and ethanol again. The product showed very poor solubility both in CDCl_3 and DMSO-d_6 and it was not possible to take an ^1H NMR. We also could not obtain a mass spectrum. The yield of the reaction was 81.4%.

$\lambda_{\text{max}} = 538\text{nm}$ (in ethanol with K_2CO_3)

Synthesis of 9-Cyano-2-octanoyl-4,5,7-triiodo-3-hydroxy-6-fluorone (10:R=n-C₇ H₁₅)

2-Octanoyl-4,5,7-triiodo-3-hydroxy-6-fluorone (0.1mmol) was dissolved in 3ml of DMF, KCN (0.3mmol) added and the mixture was stirred for 1 hour at room temperature. The mixture was then poured into a dilute solution of HCl (carefully!) forming a purple precipitate which was filtered and washed with water giving 9-cyano-2-octanoyl-4,5,7-triiodo-3-hydroxy-6-fluorone in 88% yield. This compound had very good solubility in CDCl_3 and the NMR is consistent with the assigned structure.

^1H NMR (CDCl_3): 13.93ppm(1H, s), 8.23(1H, s), 8.13(1H, s), 3.15(2H, t, 7.3Hz), 1.7-1.9(2H, m), 1.2-1.6(8H, m), 0.94(3H, t)

$\lambda_{\text{max}} = 636\text{nm}$ (in ethanol with K_2CO_3)

Synthesis of 2-Octyl-3,6-dimethoxyxanthane (11: R=n-C₇ H₁₅)

2-Octanoyl-3,6-dimethoxyxanthane (2mmol) was dissolved in a mixture of 15ml of ethanol, 16ml of dichloromethane, 1ml of water and 0.6ml of conc. HCl. To this mixture was added 0.6g activated carbon containing 10 wt% of palladium. After stirring overnight under an atmosphere of hydrogen, the activated carbon was filtered and washed with chloroform. The organics were then washed with water in a separatory funnel. The organic solvents were removed under reduced pressure and the remaining compound was purified using column chromatography yielding 83.4% of 2-octyl-3,6-dimethoxyxanthane.

¹H NMR (CDCl₃) : 7.05ppm(1H, d, 8.8Hz), 6.88(1H, s), 6.60(1H, dd, 8.3Hz, 2.4Hz), 6.58(1H, s), 6.54(1H,s), 3.90(2H, s), 3.80(6H, s), 2.54(2H, t, 7.2Hz), 1.2-1.4(12H, m), 0.9(3H,t)

MS m/e for C₂₃H₃₀O₃ calcd; 354.49 measured; 354.15

Synthesis of 2-Octyl-3,6-dihydroxyxanthane (12: R=n-C₇ H₁₅)

2-Octyl-3,6-dimethoxyxanthane (1.2mmol) was dissolved in a mixture of 5ml of ethanethiol and 20ml of anhydrous dichloromethane. After cooling in a dry ice/EtOH bath, aluminum chloride (6mmol) was added. The reaction mixture was stirred gradually, allowed to come to room temperature overnight, and then poured into a mixture of 20g of ice and 10ml of conc. HCl. The dichloromethane layer was separated and the solvent removed under reduced pressure. The residue was dissolved in an aqueous NaOH solution which was next poured into dilute HCl to obtain a precipitate. The precipitate was filtered, washed with water to yield product (93.9%). ¹H NMR suggested that the compound was a mixture of 2-octyl-3,6-dihydroxyxanthane (77%) and an oxidized fluorone form (23%). Further purification was not attempted because both compounds yielded the same compound in the next step.

¹H NMR in CDCl₃/DMSO=10/1 (only for the aromatic ring)

6.96ppm(1H, s), 6.82(1H, s), 6.50-6.52(3H, m), 3.82(2H, s)

Oxidized form: 7.96ppm(1H, s), 7.53(1H, d, 9.3Hz), 7.41(1H, s), 6.92(2H, s), 6.71(1H, s)

mp = 130-135°C

Synthesis of 2-Octyl-4,5,7-triiodo-3-hydroxy-6-fluorone (13: R=n-C₇ H₁₅)

2-Octyl-3,6-dihydroxyxanthane (0.3mmol) and iodine (0.3mmol) were dissolved in 3ml of ethanol. An aqueous solution of iodic acid (0.3mmol in 0.2ml of water) was added at room temperature, the reaction mixture brought to reflux, and stirred for 1 hour. The resulting red precipitate was filtered, and washed with an ethanol and water mixture to obtain 2-octyl-4,5,7-triiodo-3-hydroxy-6-fluorone in 70.6% yield.

^1H NMR (DMSO) : 8.45ppm(1H, s), 8.20(1H, s), 7.61(1H, s), 2.67(2H, t, 7.6Hz), 1.5-1.6(2H, m), 1.1-1.4 (10H, m), 0.85(3H, t, 6.6Hz)

$\lambda_{\text{max}} = 532\text{nm}$ (in ethanol with K_2CO_2)

Synthesis of 9-Cyano-2-octyl-4,5,7-triiodo-3-hydroxy-6-fluorone (14: R=n-C₇ H₁₅)

2-Octyl-4,5,7-triiodo-3-hydroxy-6-fluorone (0.135mmol) was dissolved in 3ml of DMF. To the solution was added KCN (0.5mmol) and the reaction mixture stirred at room temperature. The conversion was monitored with spectrometer. After 2 hours, the mixture was poured (careful!) into dilute HCl. The organic compounds were extracted with chloroform, and the chloroform solution washed with water several times to remove DMF. The chloroform was removed yielding 73.2% of 9-cyano-2-octyl-4,5,7-triiodo-3-hydroxy-6-fluorone .

^1H NMR (DMSO) : 8.14ppm(1H, s), 7.44(1H, s), 2.64(2H, t, 7.0Hz), 0.8-1.6(15H, m)

λ_{max} (in EtOH with K_2CO_2)=630nm

Absorption and Fluorescence Measurements:

Absorption spectra were obtained using a Hewlett Packard 8452A diode array spectrophotometer and ethanol as the solvent. Figure 1 shows the absorption spectrum of DIBF in ethanol.

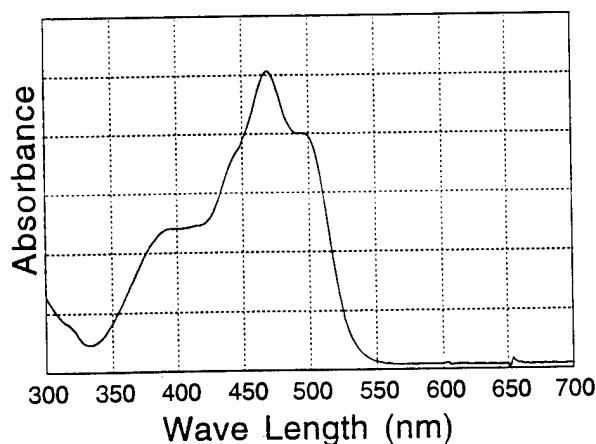


Fig 1 Absorption Spectrum of DIBF in ethanol

Quantum yields of fluorescence were measured using a SPEX-FLUOROLOG II spectrometer relative to rhodamine 6G in ethanol. The results are summarized in Table 3.

Photopolymerization of acrylic monomers:

The monomers or oligomers used were: a) Polyethylene glycol-400 diacrylate, PEGA-400, from Monomer-Polymer Laboratories, Inc.; b) Trimethylolpropane triacrylate, TMPTA, Saret 351, from Sartomer Co.; c) Dipentaerythritol pentaacrylate, DPHPA, Sartomer 399, from Sartomer Co. Stabilizers were not removed because it has been observed that this generates an instability in the reaction mixture with polymerization starting before it is really intended. The measurement of the mechanical properties of the materials obtained from photopolymerization is much more accurate if the monomers are used as received. The composition of the basic monomer mixture utilized for most experiments consisted of, in weight percent, PEGA (20), TMPTA (40), DPHPA (40). The mixture of these three monomers formed the basic standard resin used and it is henceforth referred to as STDR.

Mechanical properties of polymers:

The dyes used as photoinitiators for comparison studies of the mechanical properties of photoformed polymers were 3-ethoxy-5,7-diodo-3-fluorone (DIEF), 3-butoxy-5,7-diodo-6-fluorone (DIBF, 3a), and 3-octoxy-5,7-diodo-6-fluorone (DIOF, 3b). All were used in a concentration of 2×10^{-4} M both for the mechanical property studies and for the determination of the percentage double bond conversion (% C=C). N,N-dimethyl-2,6-diisopropylaniline, DIDMA, [5×10^{-2} M] from Carbolabs, Inc. was used as the coinitiator.

Each dye (sensitizer) was first dissolved in pure PEGA and the solution submitted to ultrasound for about 15 minutes after which the other multifunctional acrylates, TMPTA and DPHPA, were added to the system and the whole mixture was again submitted to ultrasound for an additional 20 minutes. DIDMA, the co-initiator, was the last substance added to the to be reacted mixture, and it was added immediately before irradiation.

This photoreactive mixture was poured into dogbone-shaped Teflon molds, 2.0 mm deep, 6.0 mm wide, with a gauge length of 70.0 mm, and a total length of 150.0

mm. These dimensions do not strictly follow the specifications of the ASTM-D638-82a norm but they are certainly suitable for comparison of the relative mechanical strength of the photopolymers formed under the small changes in composition studied.

Irradiation was carried out in air. An Ar⁺ laser (Omnichrome, model 543-200 MGS) was used as the irradiation source. The laser beam was directed toward the sample by mirrors positioned above the Teflon molds. These mirrors were controlled by *x-y* scanners (DX-series servo controller, from General Scanning, Inc.) to form the dog-bone-shaped parts. The mirrors were driven by digitized computer data from a special file initially designed to generate a solid cube. If the *z* (vertical) transition is neglected, the file just controls the laser beam to generate a square. The file scale option was appropriately modified to span a little more than a 200.0 x 200.0 mm square region which is large enough to include all the dog-bone-shaped molds with the photosensitive mixtures. Laser power used was fixed at 100.0 mW. Beam diameter was typically 2.0 mm. The speed control option of the file used was such that the laser beam was scanned over the samples at a speed of about 9.0 mm/sec.

Mechanical Properties Measurement:

Stress-strain tests were carried out at ambient temperature (typically 23°C), with no strict humidity control, using the photopolymerized dog-bone-shaped samples prepared as described. The tests were performed using an L-500 instrument from Lloyd Instruments, Fareham, England, fitted with an NLC-500N load cell. The crosshead speed used was the slowest possible with this machine, 5.0 mm/s; the sample gauge length was 70.0 mm, and the width was 6.0 mm.

The instrument was controlled by an MCM-4135T Goldstar PC booted with Lloyd's DAPMAT software. This analysis program allowed direct observation of the load versus elongation behavior of the sample during the tests. After the test ended, it also automatically displayed various physical parameters of interest, including stress at break, (N·mm⁻²) and elongation at break, (absolute, in mm, and relative in

%), maximum load (N), work performed (N·mm) and Young's modulus of elasticity (N·mm⁻²), among others. The results are summarized in Table 1.

Double bond conversion measurement with FTIR :

For the percentage of double bond conversion, %C=C, a few drops of the photoreactive mixture were squeezed between sodium chloride (NaCl) windows using a 15.0 μm thick Teflon spacer. FTIR spectra were taken using a Galaxy Series 6020 spectrometer from Mattson Instruments, Inc. The spectra were taken before and after irradiation and the areas corresponding to an acrylic bending mode at 810 cm^{-1} were used for the calculation¹⁸:

$$\%C=C = S_0 - S_1 / S_0$$

where S_0 and S_1 are the areas corresponding to the 810 cm^{-1} band before and after the irradiation, respectively. The same laser scanning procedure used for the mechanical properties experiments was used for the percentage of double bond conversion determination. The samples were irradiated only after a sequence of spectra were obtained and the difference between the S_0 areas differed by less than 5%. The final result corresponds to an average of at least two measurements for each sample. The results are summarized in table 1 and table 2.

Results and Discussion:

Several characteristics are important targets in designing visible dyes of greater reactivity as photopolymerization initiators. First, extending the dye absorption to the red and near-IR region of the electromagnetic spectrum is of significant practical importance, and significant structural changes are being sought in order to considerably increase the electronic delocalization of the π system and extend the λ_{max} . This will be the main topic of a separate report. Also, solubility in monomer has always been one of the most important topics in consideration for the effective

use of these dyes as photoinitiators for acrylate, epoxies, and other types of resins. Much of the work reported herein is driven by that consideration. Since most of the resins of choice are apolar substances, solubility has been considerably improved by adding large hydrocarbon side chain to the 3-positioned oxygen of the 6-fluorone structure. Considerable increase in solubility has also been observed when changing from DIEF to DIBF which have an ethyl or a butyl group, respectively. However, the improvement did not seem to continue when moving from a 4-carbon side chain, DIBF, to an 8-carbon side chain, DIOF, and the addition of a long side chain to the basic fluorone structure has only a minor influence on the photophysical behavior of the dyes as initiators.

In order to compare the efficiency of different photoinitiators, two principal tests were performed. First the percentage of carbon-carbon double bonds converted to single bonds by the photopolymerization process was determined using the well established FTIR method¹⁹. Then, dogbone samples were made using the same basic acrylic resin, and the stress-at-break, σ , and Young's modulus of elasticity, Y , were determined by stress \times strain measurements. Table 1 presents the results of these tests using DIEF, DIBF and DIOF as photoinitiators. The values of the mechanical properties correspond to an average of measurements over 4 samples. The dye concentration was maintained at a relatively low value (2×10^{-4} M, compared to $1-2 \times 10^{-3}$ M normally employed) to assure that a possible solubility difference had no influence in the results. The results from Table 1 show that both the % C=C and the mechanical properties improve when changing from DIEF to DIBF. However, as observed qualitatively for the solubility, the efficiency of dyes with longer side chains, like DIOF, does not seem to improve proportionally to the chain size. This result was initially surprising mainly because of the expected effect of the side chain in the dye aggregation²⁰. However, the apparent decrease in the % C=C and degradation of the mechanical properties seem to indicate that other factors may be influencing the behavior of the dyes as photoinitiators. Since no experiments have

been performed, so far, to address this issue, little can be said about specific reasons for these observations. However, it is our belief that, similarly to the phenomenon of side-chain crystallization, well known and established in polymer science²¹, side chains beyond a certain length may increase aggregation instead of avoiding it. This may be a possible explanation for the decrease in polymer performance when using DIOF as photoinitiator.

The efficiency of the fluorone dyes as photoinitiators depends on two basic factors. First, it depends on the yield of triplet state formation, which is inversely related to the fluorescence quantum yield of the dye. As has been shown before¹⁸ the fluorescence quantum yield, Φ_f , seems to be a good parameter for comparing the dye's efficiency as photoinitiator. However, this comparison holds well only if the difference between the fluorescence quantum yield is significant. This does not seem to be the case with the so-called branched dyes. The fluorescence quantum yields of all of them are very small, comparable to DIEF, and do not differ significantly. This is likely so because the difference in photoinitiating efficiency of the branched dyes is that the value $1-\Phi_f$ does not correspond directly to the yield of triplet formation, Φ_t . The value $1-\Phi_f$ is actually a sum of the fraction of molecules that have undergone intersystem crossing (ISC) to the triplet state, plus the fraction of molecules that have undergone internal conversion (IC) to high vibrational levels of the ground electronic state. The yield of triplet formation is the important factor, since it is to the triplet state of the dye to which the amine will transfer an electron during the initial steps of the photoinitiating process. Φ_t has not yet been determined for the branched dyes. Second, initiator efficiency depends on the reduction potential of this triplet state in reactions in which the dye is reduced (Scheme 1) and the overall electron transfer rate from the amine donor. If these values are known for two different dyes it is possible to predict their performance as photoinitiators according to the mechanism described in Scheme 1. Another possible factor that may be relevant however, is that when comparing the efficiency of photopolymerization of branched

dyes, the efficiency is not only related to a thermodynamic driving force for the electron transfer process, but it is also related to a kinetic contribution. The thermodynamic contribution is established by Weller's equation:

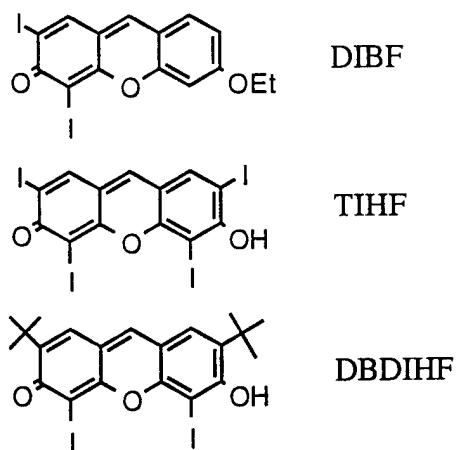
$$\Delta G_{ET} = F [E^{ox} (D/D^+) - E^{red} (A/A^-)] - E_s + \Delta E_c$$

where F is Faraday's constant, E^{ox} and E^{red} are the redox potentials of the donor and the acceptor, respectively, E_s is the excitation state of the reactive state of the dye, $E_s = hv$, and ΔE_c is the Coulomb stabilization energy. From spectroscopic and preliminary photophysical observations each branched dye will make almost the same thermodynamic contribution to the electron transfer. However, as it seems also to be the case in many other chemical processes, thermodynamic analysis does not establish guidelines for the rate with which the process will proceed. Assume, as a first approximation, that the electron transfer process obeys an Arrhenius-type equation :

$$k = A \exp - (E_a / kT)$$

where E_a is the activation energy, or an energy barrier, for the electron transfer process to occur. It is likely that each branched dye will have different E_a values because of the different groups present in their 6 position. These factors may well contribute differently to the kinetic component of the photoinitiating efficiency.

If there is a considerable difference between the fluorescence quantum yield of the dyes this single photochemical parameter seems to be sufficient to establish the initiator efficiency order. This is the case when DIEF, TIHF, and DBDIHF (2,7-di-t-butyl-4,5-diodo-3-hydroxy-6-fluorone) are compared¹⁸. The fluorescence quantum yields are 0.004, 0.13 and 0.36, respectively, and this is also the order of photoinitiator efficiency with DIEF performing best.

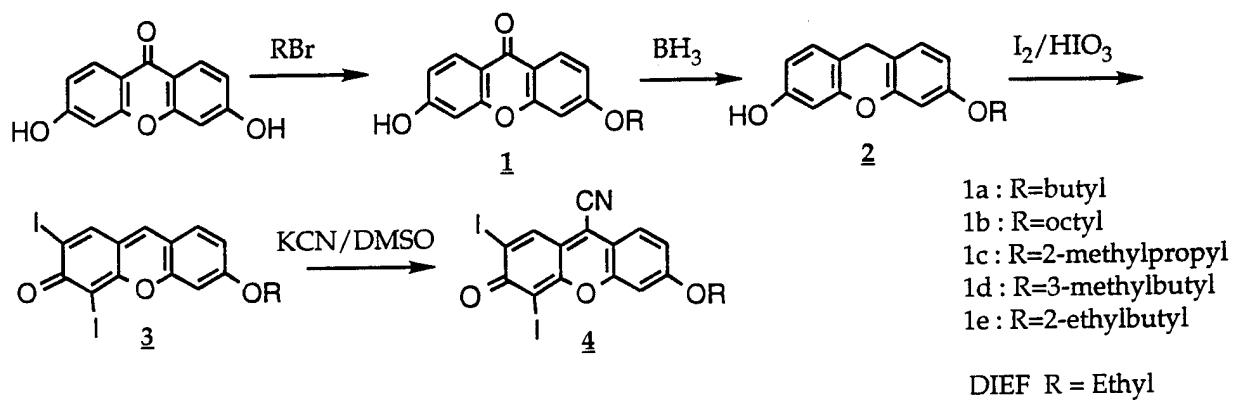


When the 3-substituent is a branched alkoxy group however, the dye's performance as a photoinitiator is more complicated. Table 2 summarizes % C=C conversion with dyes with branched 3-substituents as the photoinitiators using a dental lamp as the light source. The dye with a 2-methylpropyl group, (3c), showed poorer % C=C conversion even though it had as the same solubility in the standard monomer mixture as did DIBF. The dye with 3-methylbutyl group (3d), on the other hand, showed almost the same % C=C conversion as DIBF although the solubility was also poor. When 2-ethylbutyl group was the 3-substituent, both % C=C conversion and solubility were better than DIBF.

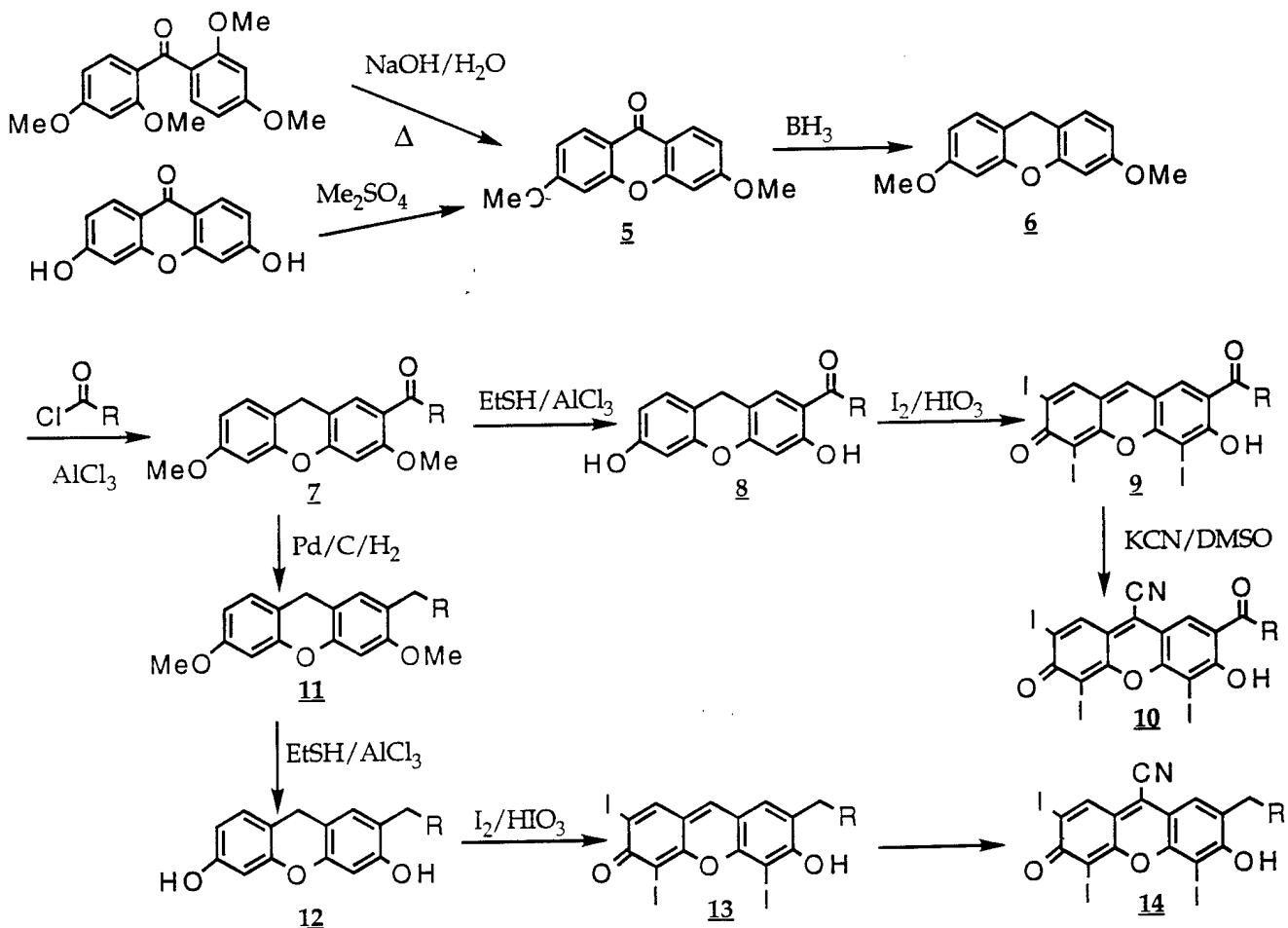
The fluorescence quantum yields of all dyes were determined and the values shown in Table 3. All have lower fluorescence quantum yields than DIBF, but there seems to be little difference between them, and that they have different performances as the photoinitiators indicates that another factor is operational. All photophysical parameters were measured in EtOH, but performances as photopolymerization initiators were obtained in acrylic monomers. Polarity differences of these rather different solvent systems might be important. This will be the subject of future investigations.

Acknowledgements: Financial support by the Office of Naval Research (Navy: N00014-93-1-0772), the National Science Foundation (DMR-9013109) and Spectra

Group Limited (SGL) is gratefully acknowledged. We are also grateful to Tom Marino of SGL, Inc. for helpful discussions.



Scheme 3



Scheme 4

Table 1 Comparison of Dye Performances on Photopolymerization

	DIEF	DIBF (3a)	DIOF (3b)
% C=C a)	27.0 ± 1	35.0 ± 1	29.0 ± 1
σ (N.mm-2) b)	2.4 ± 0.1	4.1 ± 0.2	2.7 ± 0.4
Y (N.mm-2) b)	31.6 ± 1.5	67.4 ± 4.4	49.3 ± 4.6

a) Ar⁺ laser was irradiated through NaCl window at the same condition as applied for the preparation of the sample for mechanical properties measurement.

b) Standard resin formulation: PEGA (20), TMPTA (40), DPHPA (40); Dye concentration : 2x10⁻⁴ M ; Donor : DIDMA at a concentration of 5x10⁻² M

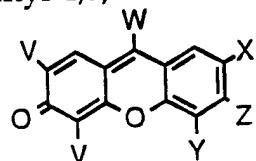
Ar⁺ laser (100.0mW, 2.0mm diameter) was scanned at a speed of 9.0mm·sec⁻¹ to make a dog-bone-shape test piece (gauge length: 70.0mm, width : 6.0mm, thickness : ca. 2.0mm). Crosshead speed was 5.0mm/s.

Table 2 % C=C Conversion with Branched Alkoxy Substituted Dyes

Dyes	3c	3d	3e	3a(DIBF)
% C=C a)	54	65	81	68
solubility in the standard monomer mixture	good	poor	excellent	good

a) Dental lamp was used as the light source.

Table 3 Photoproperties of 3-alkoxy-5,7-diodo-6-fluorones and 2-acyl or 2-alkyl-4,5,7-triiodo-6-fluorones^a



V	W	X	Y	Z	λ_{max} (nm)	ϵ	λ_{fl} (nm)	Φ_{fl}	dye
I	H	I	I	OH	536	91200	548	0.13	TIHF ¹²
I	CN	I	I	OH	638	80000	654	0.02	TICHF ¹²
					586	35000			
I	H	H	H	OMe	470	23500	544 568	0.03	DIMF ¹²
I	H	H	H	OEt	470	21100		0.058	DIEF ¹²
I	H	H	H	OBu	470	30200		0.020	3a
I	H	H	H	OOC	472	31600		0.024	3b
I	H	H	H	OC ₄ H ₉	470	22300		0.015	3c
I	H	H	H	OC ₅ H ₁₁	470	25500		0.010	3d
I	H	H	H	OC ₆ H ₁₃	472	26600		0.015	3e
I	CN	H	H	OBu	524				4a
I	H	CO ₂ C ₇ H ₁₅	I	OH	538	84800			9
I	CN	CO ₂ C ₇ H ₁₅	I	OH	636 590	17100 9900			10
I	H	C ₈ H ₁₇	I	OH	534	92600			13
I	CN	C ₈ H ₁₇	I	OH	630 580	40100 23300			14

a. All spectra were measured in EtOH. Potassium carbonate was added (Z = OH) to assure complete ionization.
Rhodamine 6G was the fluorescence quantum yield standard.

References:

¹Permanent Address: Japan Synthetic Rubber Co., Ltd., 11-24, Tsukiji 2-chome, Chuo-ku, Tokyo 104, JAPAN
²Publication # from the Center for Photochemical Sciences
³Cycolor®: Mead Imaging, Miamisburg, OH.
⁴Commercial examples are manufactured mainly by ICI, Runcorn, UK.
⁵Ciba-Geigy AG, Marly, Switzerland
⁶Typical are the ketocoumarins manufactured by Eastman Kodak.
⁷For background information see Neckers, D. C., *Mechanistic Organic Photochemistry*, Reinhold Publishing Company, New York, 1967. Chapter 7.
⁸Oster, G., *Nature*, 1954, 173 300; See, D.F. Eaton, *Advances in Photochemistry*, 13 1986, 427-486, D.H. Volman, G.S. Hammond, K. Gollnick eds., Wiley N.Y.
⁹For a review of the xanthenes in photopolymerization see Valdes-Aguilera, O. and Neckers, D. C., *Advances in Photochemistry*, Wiley, NY, Vol. 18. pp 313 - 394 (1993).
¹⁰G. Oster, U. S. Patents 2,850,445 (1958); 2,875,047 (1959); 3,097,096 (1963).
¹¹O. Valdes-Aguilera, C. P. Pathak, J. Shi, D. Watson and D. C. Neckers, *Macromol.*, **1992**, 25, 341.
¹²J. Shi, X. Zhang and D. C. Neckers, *J. Org. Chem.*, **57**, 4418, 1992; J. Shi, X. Zhang and D. C. Neckers, *Tet. Letters*, **34**, 6013, 1993.
¹³T. L. Marino, Dustin B. Martin, and D. C. Neckers, *Radtech Proceedings* **1**, 169, 1994.
¹⁴See, for example, E. Klimtchuk, M. A. J. Rodgers and D. C. Neckers, *J. Phys. Chem.*, **96**, 9817, **1992**
¹⁵S. Hassoon and D. C. Neckers, in preparation.
¹⁶S.M. Linden and D.C.Neckers, *J. Photochem. Photobiol. A: Chem.*, **1988**, 47, 543; S.M. Linden and D.C.Neckers, *J. Am. Chem. Soc.*, **1988**, 110, 1257.
¹⁷Y. Bi and D. C. Neckers, *Macromol.*, **1994**, 27, 3683.
¹⁸Afranio Torres-Filho and D.C. Neckers, *J. App. Poly. Sci.*, **51**, 931, 1994
¹⁹C. Decker and K. Moussa, *Macromol.*, **1988**, 189, 2381
²⁰O. Valdes-Aguilera and D. C. Neckers, *Acc. Chem. Res.*, **1989**, 22, 171
²¹R.W. Sorenson and T.W. Campbell, *Practical Polymer Chemistry*, 2nd ed., Interscience Publishers, New York, New York, 1968